

KINETICS OF PELLET REDUCED BY H₂ AND THE MIXTURE OF CO AND H₂

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Canadian hematite acid pellet with low magnetite and olivine contents were isothermally reduced by hydrogen and carbon monoxide at 600 to 1 000 °C. Pellet reduction was investigated by a thermo gravimetric analysis measuring oxygen weight loss as a function of time. Then macroscopic and microscopic examinations, X-ray and carbon analyses were also used to elucidate the mechanisms of pellet reduction. Activation energy is around 27 kJ/mol for H₂ atmospheres and is about 15 kJ/mol for the mixture of H₂ and CO. Carbon producing from CO disproportionation reaction performs a catalyzer at the final reduction of pellet.

Keywords: iron, direct reduced, H₂-CO mixture thermo gravimetric analysis, X-ray examination

INTRODUCTION

In the past decades, direct reduction (DR) has become a significant new process for ironmaking. About 80 % of direct reduced iron (DRI) in the world is produced by the Midrex and HYL shaft furnace processes which use syngas as reducing agent. However, one of the most serious problems encountered with a gaseous shaft furnace is kinetics of syngas on the reduction of iron oxides in a CO-H₂-CO₂-H₂O atmosphere. This unintentional change of kinetics always determines energy consumption of the ironmaking procedure.

Reduction of iron oxide and various ores containing iron oxide have been studied in the past. Various controlling mechanisms have been suggested in these studies. Hancock et al.[1] suggested a random nucleation mechanism for the reduction of Kaolinite and Brucite where phase boundary mechanism was evoked from Sastri et al.'s[2] research. El-Geassy's[3] and Moon et al.[4] worked on the reduction of hematite at temperatures ranging between 1 173 and 1 473 K and concluded that the reduction of hematite to wustite is controlled by a mixed reaction mechanism in the early stages followed by interfacial chemical reaction, while the reduction of wustite to iron is controlled by a mixed chemical reaction. The above illustrates that neither of two studies was found to have the same mechanism for iron ore reduction due to the differences of experiment conditions and physical and chemical properties of iron ore material among the investigations. Moon and Rhee [4] concluded that reducing reaction rate of hematite by H₂ was 2 to 3 times higher than that by CO atmosphere. Furthermore, apparent activation energy of iron oxide

reduction is 14,6 kJ/mol in a CO mixture and is 19,8 kJ/mol in pure CO atmosphere.

Although above numerous studies have been devoted to the evaluation of the kinetics of iron ore reduction by CO, H₂ or their mixtures as well as the effect of syngas components on reduction, there are uncertainties such as kinetic mechanism of pellet with different syngas components, microstructure evolution of pellet during reduction. The usefulness of many of these studies is limited due to the wide diversity of experimental conditions.

The purpose of the present is to carry out thermo-gravimetric analysis (TGA) of the reduction of Fe₂O₃ pellet to study the kinetics and micro/macrostructure of pellet during reduction. The second section of the paper introduces experimental method, procedure and parameters, while the third section describes the experimental results and discussion. The final section presents some conclusions of the studies.

RAW MATERIALS AND REDUCING GAS

Canadian hematite acid pellet with low magnetite and olivine contents were used in experiments. Chemical composition and physical properties of the pellet are shown in Table 1. Patterns of X-ray diffraction (XRD) and micro/macrostructure of pellet are illustrated in Figures, 1 and 2, respectively. The above properties of pellet illustrate that pellet has porous microstructure (C.F. Figure 2(b)), higher hematite and amount of SiO₂ which is related with olivine. CO, CO₂, H₂ and the mixture of CO and H₂ were used as reducing gas, while Ar and N₂ were used as an inert gas in order to prevent unexpected reactions taking place during the heating and cooling periods of the experiments. Furthermore, the purity of CO, CO₂, H₂Ar and N₂ is all higher than 99,99 %.

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EXPERIMENTAL APPARATUS AND PROCEDURE

Thermogravimetric analysis (TGA), made from Cahn TherMax 700, USA Thermo Cahn, Inc, is used to study reduction kinetics of pellet and shown in Figure 3. The apparatus is composed of a gas supply system, temperature control system and a balance which has readabilities ranging from $1\mu\text{g}$ to 100 gram and connects to a computer. The maximum temperature of furnace can reach to $1\,700\text{ }^\circ\text{C}$ by Platinum rhodium thermocouple. An alumina crucible with 26 mm height, 16 mm inner diameter and 19 mm outer diameter is used and holds the sample with 100 g pellet in experiment. The furnace has 31,5 mm inner diameter and 38 mm outer diameter with 310 mm height. Constant temperature of furnace is around 300 mm height in the furnace.

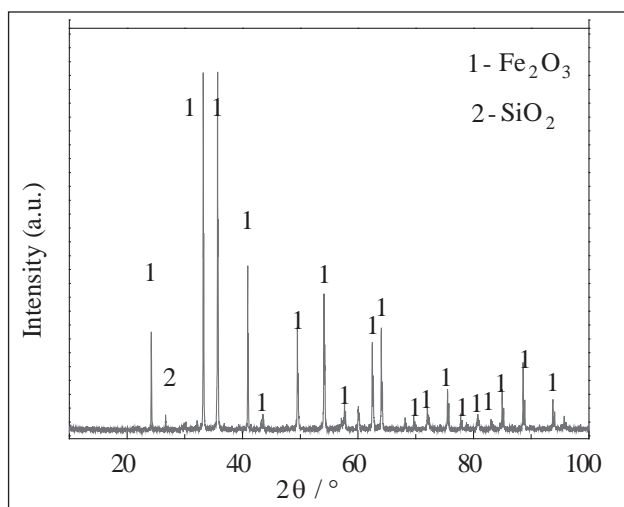


Figure 1 XRD patterns of pellet particle

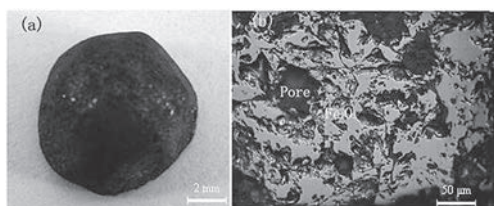


Figure 2 Photographs of pellet (a) Macro-shape (b) Microstructure by Scanning electron microscope

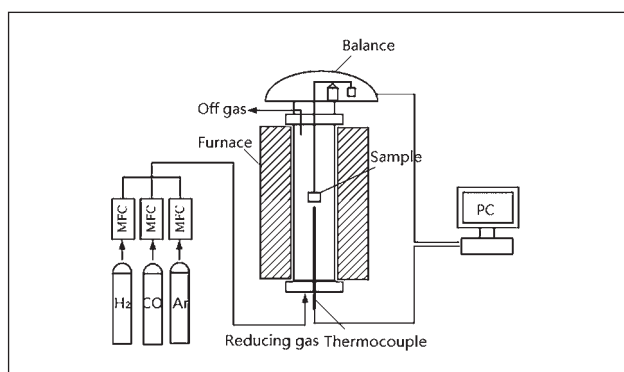


Figure 3 Schematic of experimental thermo gravimetric apparatus

Before experiment, a pellet in crucible was placed into the constant temperature region of furnace by lifting and hanging it from the balance. X-ray diffraction from Bruker D8 and SEM (JSM-6700F) from JEOL Company are used to analyze the phase and microstructure characteristic of pellet sample. Metalloscope (Leica DM6000M) illustrates the metallographs in pellet.

KINETIC MODEL OF PELLET REDUCTION

Based on the previous investigation results, pellet reduction is supposed to happen from the surface to the core. Therefore, a shrinking unreacted core model suggests to elucidate pellet reduction. In the beginning, pellet particle assumes to have 100 % hematite and has an initial diameter (r_0). With the increase of reduction reaction, there is a product layer of iron and the unreacted core of pellet particle decreases to a smaller diameter (r). Chemical reducing reaction of pellet can be separated into the following 3 stages: external diffusion, internal diffusion and chemical reaction.

The previous studies summarizes kinetic models for iron oxide reduction in various reducing atmospheres reported in the literature. The studies of kinetic parameters came from the specific conditions and indicate that there are differences about the control stage of iron ore reduction and the kinetics can apply in a narrow region.

But temperature from 600 to $700\text{ }^\circ\text{C}$ and 900 to $1\,000\text{ }^\circ\text{C}$ has more influence on reduction fraction than one from 700 to $900\text{ }^\circ\text{C}$ due to the formation of $\gamma\text{-Fe}$ on the surface of grains or more dense microstructures. Ei-Geassy[5] also found the similarity in pure H_2 reduction experiments of pellet.

RESULTS AND DISCUSSIONS

Pellet reduction behaviors by pure CO and pure H_2

Effect of temperature on pellet isothermal reduction by pure H_2 is plotted in Figure 4, All of curves increase

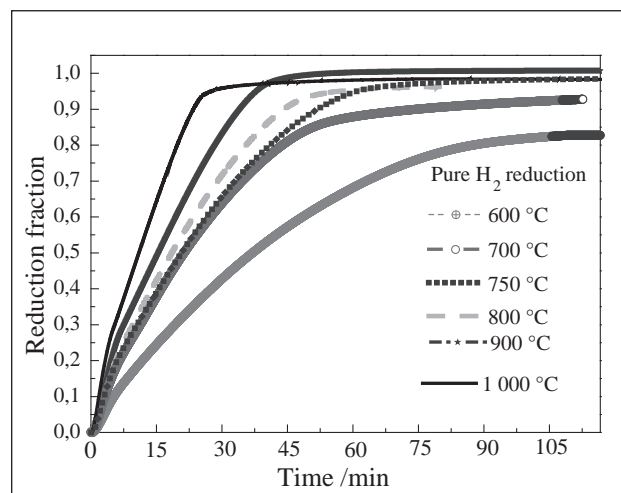


Figure 4 Thermo gravimetric curves of pellets isothermal reduced by pure H_2 at different temperatures

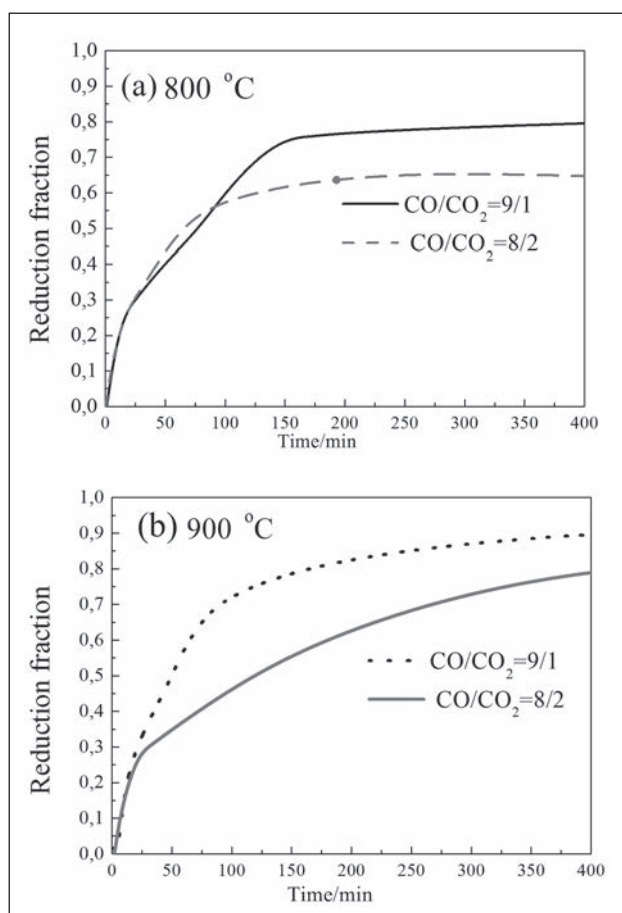


Figure 5 Effect of CO concentration on the reduction process of pellet (a) 800 °C and (b) 900 °C

Table 1 Composition and physical characteristics of pellet / wt. %

T _{Fe}	FeO	CaO	MgO	Al ₂ O ₃	S	P
62,57	0,56	2,65	0,78	1,25	0,02	0,02
SiO ₂	MnO	Size/mm		Density / kg/m ³		
5,73	0,21	10 - 12		4 950		

with the time and reach to a constant after some reduction time which indicates reduction rate is fast in the beginning and decreases to a small constant in the end. As the increase of temperature, reduction fraction becomes bigger, which means reduction rate also increase meanwhile.

Figure 5 shows effect of CO content and temperature on pellet reduction behaviors. In the beginning of reduction fraction (< 0,3), reduction rate is fast, whatever the gas components and temperature, which is consistent with H₂ effect. After 100 min, reaction rate increases with the increase of CO component in mixture and temperature. However, carbon deposition increases with increase of CO component and decrease with the increase of temperature in inserted figure of Figure 5(b). This indicates CO content stimulates carbon deposition behaviors in pellet reduction procedure.

Kinetics of pellet reduction

Figure 6 and 7 shows TGA curves and fitted curves for pellet reduction in pure H₂ refer to Figure 4 where

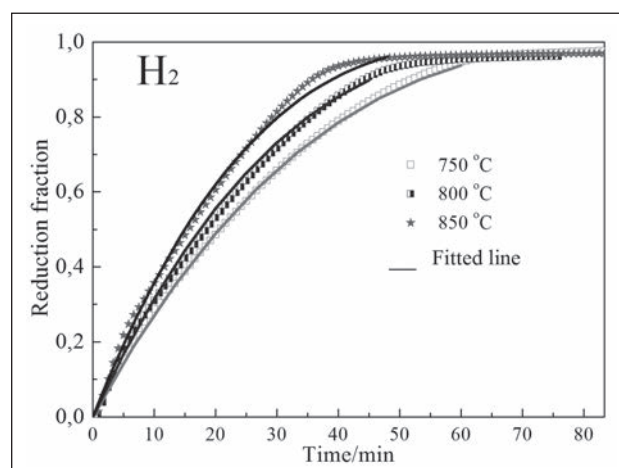


Figure 6 TGA curves and fitted curves for pellet reduction in pure H₂ refer to Figure 4

Table 2 Apparent activation energy (AAE) fitting results for Fe₂O₃ → Fe by phases

Reduction stage	Contents	AAE E _a / (kJ/mol)	R ²
Fe ₂ O ₃ → Fe ₃ O ₄	H ₂	26,4	0,97
Fe ₃ O ₄ → FeO	H ₂	27,48	0,95
FeO → Fe	H ₂	28,15	0,99
Fe ₂ O ₃ → Fe ₃ O ₄	H ₂ -CO	6,83	0,98
Fe ₃ O ₄ → FeO	H ₂ -CO	10,38	0,99
FeO → Fe	H ₂ -CO	14,92	0,96

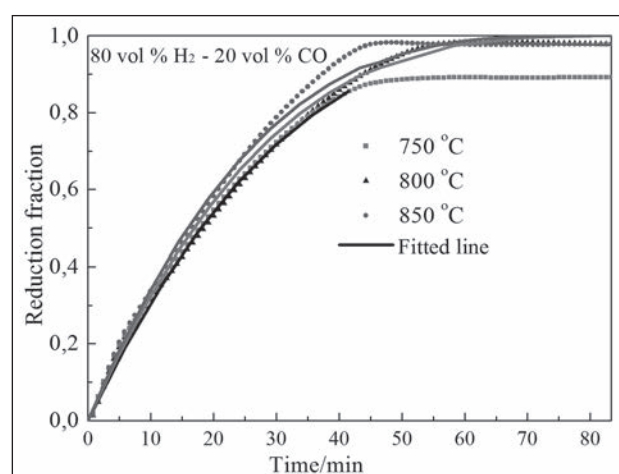


Figure 7 TGA curves and fitted curves for the iron ore reduction

fitting curves have good correlation with experimental ones. The apparent activation energies of pellet reduced by H₂ atmosphere and H₂-CO mixture atmosphere are plotted in Figure 7 and Table 2, Interfacial chemical reaction is highest correlation coefficient curves (R² = 0,99) than external diffusion and internal diffusion, which indicates that chemical reaction control the whole reduction process.

CONCLUSIONS

The present work has used thermo gravimetric analysis to investigate reduction behaviors of pellets and

study macrostructure and microstructure of pellet particle in reduction. The following conclusions can be drawn.

CO content in mixture can stimulate carbon deposition behaviors in pellet reduction procedure and carbon deposition leads to the fracture of pellet at the low temperature. Pellet reduced by CO has porous structures, while pellet reduced by H_2 has a dense product layer on the surface. At the final reduction, carbon produces from CO disproportionation reaction with Fe as a catalyst.

Acknowledgments

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Note: The responsible for English language is: S. Geng, Shanghai, China